

CLASSIFICATION

SECRET

SECRET

CENTRAL INTELLIGENCE AGENCY
INFORMATION FROM
FOREIGN DOCUMENTS OR RADIO BROADCASTS

REPORT

50X1-HUM

CD NO.

COUNTRY USSR

DATE OF
INFORMATION 1950

SUBJECT Scientific - Chemistry, physical

DATE DIST. 16 Mar 1951

HOW
PUBLISHED Thrice-monthly periodicalWHERE
PUBLISHED Moscow

NO. OF PAGES 4

DATE
PUBLISHED 11 Dec 1950SUPPLEMENT TO
REPORT

LANGUAGE Russian

50X1-HUM

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE
OF THE UNITED STATES WITHIN THE MEANING OF ESPIONAGE ACT 50
U. S. C. 31 AND 32, AS AMENDED. ITS TRANSMISSION OR THE REVELATION
OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PRO-
HIBITED BY LAW. REPRODUCTION OF THIS FORM IS PROHIBITED.

THIS IS UNEVALUATED INFORMATION

SOURCE

Doklady Akademii Nauk SSSR (Novaya Seriya), Vol LXXV, No 5, 1950,
pp 719-721.

A NEW METHOD FOR THE DETERMINATION OF SOLUBILITY
WITH THE AID OF RADIOACTIVE INDICATORS

M. B. Neyman, B. V. Miller, and A. I. Fedoseyeva
Inst Phys Chem, Acad Sci USSR
Presented by Acad N. N. Semenov, 14 Oct 1950

The method of radioactive indicators, used in 1917 by V. I. Spitsyn ^[1] for determining the solubility of thorium salts, has been used subsequently by a number of authors in investigating the solubility of various difficultly soluble compounds. B. A. Nikitin and A. Polesitskiy determined the solubility of radium salts ^[2-4], and that of compounds of lead ^[5], cobalt ^[7, 8], and silver bromide ^[9] have been determined by the radiometric method. There is an article ^[10] which gives a review of works on the use of radioactive indicators in analytical chemistry.

A series of methods -- gravimetric, potentiometric, colorimetric, etc. -- have been developed for the determination of solubility. The gravimetric method takes a great deal of time, since it is necessary to wait for equilibrium to be established between the precipitate and the solution. It is inconvenient to use the other methods when the solubility must be determined not in water, but in concentrated solutions. But in a series of works on analytical chemistry one encounters the need for a rapid estimation of solubility not only in the pure form, but also in the presence of an excess of various ions. It is particularly important to have a method for rapidly estimating the degree of solubility in the case of the separation of radioactive materials produced by the reactions (n, p) and (n, α) when a large number of foreign ions are present. The present work proposes a method for the determination of solubility which makes possible the solution of such a problem.

Let us first examine the general theory behind the method. Let there be in the solution an unweighable quantity of ions A with a radioactivity of c impulses per minute. We will add a millimoles of the inactive ions A to the solution as a carrier. In order to precipitate the compound B in which we are

- 1 -

SECRET

CLASSIFICATION

SECRET

STATE	<input checked="" type="checkbox"/> NAVY	<input checked="" type="checkbox"/> NSRB		DISTRIBUTION								
ARMY	<input checked="" type="checkbox"/> AIR	<input checked="" type="checkbox"/> FBI										

SECRET

SECRET

50X1-HUM

interested we add the appropriate reagents D, and the volume of the solution is brought up to v_1 ml. The resulting precipitate B, containing part of the activity, is filtered and washed. The precipitate is then dried, and its activity I_1 is determined in imp/min. Part of the activity, depending on the solubility of substance B, goes into the filtrate. To this filtrate again are added a millimoles of carrier A, and substance B is precipitated a second time with reagents D. The volume of the solution is now brought to v_2 ml. The second precipitate B is filtered, washed, and dried, after which its activity I_2 is determined in imp/min. If the sought-for solubility of B is equal to x millimoles/ml, then after the first precipitation xv_1 millimoles of salt remain in the solution, while in the precipitate there are $(a - xv_1)$ millimoles.

The activity of the first precipitate I_1 , is only part of the total activity c :

$$I_1 = c \frac{a - xv_1}{a} \quad (1)$$

After the second precipitation the solution contains xv_2 , and the precipitate $a + xv_1 - xv_2$ millimoles. Clearly, the activity of the second precipitate is determined by the formula

$$I_2 = \frac{cxv_1}{a} \frac{a + xv_1 - xv_2}{a + xv_1} \quad (2)$$

The ratio of the activity of the first precipitate to that of the second is

$$\beta = \frac{I_1}{I_2} = \frac{a^2 - x^2v_1^2}{xv_1 [a + x(v_1 - v_2)]} \quad (3)$$

From this

$$x = \frac{-av_1\beta \pm \sqrt{a^2\beta^2v_1^2 + 4a^2v_1[\beta(v_1 - v_2)]}}{2v_1[v_1 + (v_1 - v_2)]} \quad (4)$$

If the precipitation is always carried out from the same volume v , then formula (4) can be simplified and reduced to the form

$$x = \frac{a(\sqrt{\beta^2 + 4} - \beta)}{2v} \quad (5)$$

With the above described method we determined the solubility of copper thiocyanate in $ZnSO_4$ solutions. Cu^{64} served as the radioactive indicator.

Although the method for the determination of copper in the $Cu_2(CNS)_2$ form is often used, we were unable to find data on the solubility of this compound. The experiments were conducted in 50% solutions of zinc sulfate into which were introduced an unweighable quantity of radioactive copper and 15 mg, i.e., 0.093 millimole, of $CuSO_4$ as a carrier. In every experiment, a precipitate was obtained from both the original solution and the filtrate. The conditions of precipitation were the same in all cases. The volume of the solution v for precipitation was always equal to 250 ml. Solubility was calculated by formula (5). The results are shown in Table 1.

- 2 -

SECRET

SECRET

SECRET

SECRET

50X1-HUM

Table 1. Solubility of $\text{Cu}_2(\text{CNS})_2$ in a Concentrated Solution of ZnSO_4 at 20°

Experiment	I_1 (imp/min)	I_2 (imp/min)	Δ	$\bar{x} \cdot 10^4$ Moles/Liter
1	4460	1950	2.3	5.2
2	7420	2640	2.8	5.0
3	15490	3550	4.35	3.8
4	645	225	2.8	5.0
5	860	272	3.16	4.1
6	817	295	2.78	4.7
Average				4.6

As the table shows, the probable error does not exceed 10%. The solubility of $\text{Cu}_2(\text{CNS})_2$ under our conditions is 0.46 ± 0.05 millimoles/liter.

The above data shows that the method proposed by us can be used for the rapid determination of solubility.

We have made attempts to use our method to study the dependence of solubility on the concentration of precipitating reagents.

It is well known that when phosphoric acid is precipitated as MgNH_4PO_4 the use of a 10-fold excess of the precipitating agent is recommended. We conducted a series of experiments to check the completeness of separation of this salt for different excesses of the precipitating agent. The experiments were conducted with an equivalent quantity of magnesia mixture, and also with 2-fold, 4-fold, and 20-fold excesses of the precipitating agent. We carried out the determination by our method and we made parallel gravimetric determinations as a control in a series of cases.

The results of our experiments are presented in Table 2.

Table 2. Solubility of MgNH_4PO_4 at 20°

Characteristic of Solution, Concentration in Moles/Liter			Radiometric Method			\bar{x} in Moles/Liter	Gravimetric Method \bar{x} in Moles/Liter
NaH_2PO_4	MgCl_2	NH_4Cl	I_1 (imp/min)	I_2 (imp/min)	Δ		
0.015	0.02	0.187	424 \pm 8	137 \pm 6	3.1	0.005	0.01
0.015	0.02	0.187	422 \pm 8	136 \pm 6	3.1	0.005	0.01
0.015	0.04	0.23	773 \pm 10	83 \pm 5	9.3	0.002	0.005
0.015	0.04	0.23	788 \pm 10	92 \pm 5	9.0	0.002	0.005
0.015	0.08	0.26	1138 \pm 12	9	126	$\sim 10^{-4}$	$\sim 10^{-4}$
0.015	0.4	0.63	1152 \pm 14	0	--	0	0

As the table shows, a 4-fold excess of the magnesia mixture is sufficient for total precipitation of the salt. Further increase of the precipitating agent does not alter the results.

- 3 -

SECRET

SECRET

SECRET

SECRET

50X1-HUM

Our experiments have shown that the gravimetric and radiometric methods give closely corresponding results.

The method proposed by us can be used not only for the determination of solubility, but also for estimation of the adsorptive capacity of an adsorbent, for the investigation of coprecipitation, and for the solution of a number of other problems.

BIBLIOGRAPHY

1. V. I. Spitsyn, ZhRFXhO, 49, 357 (1917).
2. B. A. Nikitin and O. Erbakher, Zs. Phys. Chem., A, 158, 216 (1932).
3. B. A. Nikitin and P. Tolmachev, Ibid, A, 167, 260 (1934).
4. A. Polesitskiy and P. Tolmachev, DAN SSSR, 3, 319 (1936).
5. V. P. Shvedov, E. O. Gol'dshteyn, and N. I. Seletkova, Zhurn. Analit. Khim., 3, 109 (1948).
6. H. Kishi, Bull. Chem. Soc. Japan, 10, 362 (1935).
7. B. Cacciapuoti and F. Ferla, Ann. Chim. Applicata, 29, 166 (1939).
8. B. Cacciapuoti and F. Ferla, Atti Accad. Linc., 28, 385 (1938).
9. R. Ruka and J. E. Willard, Journ. Phys. Coll. Chem., 53, 351 (1949).
10. M. B. Neyman and A. N. Nesmeyanov, Usp. Khim., 17, 401 (1948).

- E N D -

- 4 -

SECRET

SECRET